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SEPARATE IDENTIFICATION OF COPPER (II) AND ZINC (II) IN TINTED CRYSTAL GLASS

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Methods for fast determination of copper and zinc oxides as tint carrier for crystal glass are developed. The methods have been tested on samples of tinted crystal glass. The correctness of this determination has been corroborated by the atom-absorption method.

The consumer market is currently saturated with clear crystal-glass products. One of the ways of attaining a steady position on the market of crystal glass products is expanding the product range, in particular, producing crystal glass of a wide color range.

Various colorants are used to tint crystal glass. Cobalt oxide CoO is added to the batch to obtain crystal of blue-purple color. A green tint is imparted to crystal via chromium(III) compounds combined with copper(II) in a reducing medium (Cr₂O₃ and CuO). Crystal glass of "red ruby" color is produced by introducing cadmium sulfide and selenium, in which case mixed crystals of cadmium sulfoselenide CdS · CdSe are formed and impart tinting.

To control the technological process of tinted crystal production and the quality of the finished product, the present study offers fast and accessible methods for identifying the color carrier (Cu²⁺, Zn²⁺).

Analysis of crystal glass is complicated, since this is a multicomponent system. Apart from copper and zinc oxides, it contains such components as SiO₂, PbO₂, Fe₂O₃, K₂O (Na₂O), B₂O₃, and Cr₂O₃ in significantly larger quantities than the compounds of copper(II) and zinc(II) that need to be determined.

The scientific literature offers different methods for separate identification of copper and zinc, such as atom-absorption spectrometry, x-ray-fluorescent analysis, and electrochemical methods, such as potentiometry with ion-selective electrodes, and different variants of volt-amperometry, and chromatography. Titrimetric methods such as complexonometry are used as well; the indicators used are xylenol orange black eriochrome T, and "tetra." However, there are no methods for separate determination of copper(II) and zinc(II) in tinted crystal glass described in the literature.

Based on the critical analysis of the published sources [1–13] and considering the given problem, we selected the following methods for determining copper(II) and zinc(II) in tinted crystal glass: complexonometric titration and atom-absorption spectrometry.

The indicator metal selected for complexonometric titration of copper(II) was tetra-bis(4-sodium-tetrazolylazo-5)-ethylacetate ("tetra"). Tetra together with copper(II) in the interval of pH = 1–11 forms a purple-color complex. When copper in solutions with pH < 8 is titrated using complexone III in the presence of tetra, a contrasting transition of the purple color into a green color is observed. In an alkaline medium the indicator transition is less obvious [13].

The presence of cobalt, nickel, zinc, cadmium, or lead in concentrations not exceeding 2.5 mg/liter does not interfere in the complexonometric determination of copper content. Large quantities of aluminum and manganese do not interfere in the determination in an acid medium with pH < 4; Fe(III) in these conditions can be masked by fluorides. The sensitivity is 10 µg/liter [14].

Testing this method on model mixtures of compositions closed to that of tinted crystal glass demonstrated the selective determination of the content of copper(II) in the presence of 2.5 mg/liter zinc and lead. The actual content of these components in glass exceeds the specified quantity (here and elsewhere, wt.%): ≥ 18 PbO, 1.5 ± 2 ZnO. To determine the content of zinc(II) in glass, the method of complexonometric titration was used (xylenol orange was the indicator) [15]. It was established that this determination as well was impeded by substantial quantities of lead(II) and iron(III). In this context, the following scheme of separate determination of copper(II) and zinc(II) in tinted glass crystal was proposed by us.

Large quantities of lead(II) were removed in the form of sulfate with its subsequent dissolution in ammonium acetate,

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TABLE 1

Sample analyzed	Glass sample weight, g	Mass content ($x \pm \Delta x$), %	
		Cu(II)	Zn(II)
1	0.5003	0.88 ± 0.03	1.00 ± 0.07
2	0.4998	0.88 ± 0.05	1.00 ± 0.03
3	0.5000	0.89 ± 0.02	0.99 ± 0.09
4	0.5027	0.89 ± 0.04	0.99 ± 0.02
5	0.5000	0.87 ± 0.02	1.01 ± 0.03
6	0.5012	0.87 ± 0.03	1.01 ± 0.06

in accordance with OST 21-68.1-3-92. Next a saturated solution of sodium fluoride was added to one aliquot part, thus masking Fe^{3+} ions, and the sum of copper and zinc was titrated. In another aliquot part thiourea was used to mask copper, and zinc was titrated with xylenol orange. The concentration and volume of sodium fluoride and thiourea needed to fully mask Fe^{3+} and Cu^{2+} ions present in the model mixture were determined experimentally. The copper content was revealed based on the difference.

It is established that the contents of copper and zinc determined in model mixtures resembling the mixtures analyzed agree with the specified values ($\text{Sr} \leq 0.02\%$). The method for the fast separate determination of the contents of jointly present copper(II) and zinc(II) was tested by analyzing tinted crystal glass.

The method of preparing samples for analysis was as follows. A sample of finely milled glass (OST 21-68.1-92) of weight 0.5000 g was placed in a platinum cup of capacity 100 ml. Next, 1–3 ml concentrated sulfuric acid and 7–10 ml hydrofluoric acid were added. The content of the cup was evaporated to moist salts on an electric heater. The salt in the cup was dissolved in 1.0–1.5 ml concentrated sulfuric acid, and distilled water was added up to 20–30 ml. The solution was heated on an electric heater. After cooling, the precipitate in the cup was transferred onto a “blue ribbon” double filter. The cup and the precipitate on the filter were multiply washed with 5% sulfuric acid solution. The filtrate was collected into a volumetric flask of capacity 250 ml, then the volume of the solution was brought to the mark by adding distilled water and mixed.

The filtrate contained copper, zinc, and iron sulfates, and water-insoluble lead sulfate remained on the filter and its content was subsequently determined according to OST 21-68.1.

The contents of copper and zinc in tinted crystal were determined in the following way: after the sample was converted into a solution, 2 ml saturated sodium fluoride solution was added to a 50-ml aliquot part. Next, the solution was neutralized with 10% ammonium solution until the “congo” paper started to redden ($\text{pH} = 3-4$). Next, 20 ml of a buffer acetate mixture ($\text{pH} = 5.2-5.8$) and 2–3 drops of xylenol orange solution were added, and the sum of copper and zinc was titrated with 0.0025 M solution of complexone III until the crimson color changed into a yellow one.

Another aliquot par of volume 50 ml was taken, then 2 ml saturated sodium fluoride solution and 5 ml 1 M solution of thiourea were added to it. Next, the solution was neutralized with 10% ammonium solution until the congo indicator paper started reddening ($\text{pH} = 3-4$). After that 20 ml buffer acetate solution and 2–3 drops xylenol orange were added and zinc was titrated with 0.0025-M complexone III until the transition of the crimson color into a yellow one. The copper content in glass was determined based on the difference.

The mass content (%) of zinc and copper in glass was calculated based on the formulas

$$w_{\text{Zn}} = \frac{V_1 T_{\text{Zn}} V_f K}{V_{\text{al}} m} \times 100,$$

$$w_{\text{Cu}} = \frac{(V_0 - V_1) T_{\text{Cu}} V_f K}{V_{\text{al}} m} \times 100,$$

where V_1 is the volume of complexone III consumed in zinc titration, ml; T_{Zn} and T_{Cu} are the titer of the solution of complexone III for zinc and copper, g/ml; V_f is the capacity of the volumetric flask in which the sample is poured, ml; K is the coefficient of molarity of the complexone III solution; V_{al} is the volume of the aliquot part of the sample, ml; m is the mass of the glass sample, g.

The results of the determination of copper and zinc contents in tinted crystal glass are presented in Table 1. The number of determinations is 3, the confidence probability is 0.95.

It can be seen from Table 1 that the content of copper and zinc oxides in the samples of tinted glass crystal is constant. The glass samples were taken once a week from the Sputnik furnace of the Saratovstroisteklo company for several months.

TABLE 2

Tinted crystal glass	Titrimetry		Atomic absorption		F_{exp}	t_{exp}
	$x \pm \Delta x$, %	S_r	$x \pm \Delta x$, %	S_r		
Saratovstroisteklo JSC	0.88 ± 0.04 (Cu)	0.02	0.89 ± 0.07	0.04	1.500	0.06
	1.00 ± 0.08 (Zn)	0.04	1.01 ± 0.02	0.01	0.134	0.09
Gus-Khrustalnyi JSC	1.20 ± 0.02 (Cu)	0.01	1.21 ± 0.09	0.05	1.800	0.07
	1.25 ± 0.02 (Zn)	0.01	1.27 ± 0.03	0.01	0.410	0.11

Notations: F) Fisher criterion; t) Student criterion, S_r) relative standard deviation.

The correctness of the separate complexonometric determination of the content of copper(II) and zinc(II) was evaluated using the atom-absorption method (Table 2). An AAS 1 spectrometer with a slot burner was used. The resonance radiation sources were bulbs with a hollow cathode. An air-acetylene flame and the resonance lines 324.7 nm (Cu) and 213.9 nm (Zn) were used. The monochromator slot width was set equal to 0.03 nm, and the bulb current was 5 mA (Cu) and 10 mA (Zn). The device was adjusted to obtain the maximum possible reproducible signal of copper and zinc absorption. An analysis of model mixtures had previously established that the accompanying elements do not affect the process of atomization of copper(II) and zinc(II).

The results of determining copper and zinc contents in tinted crystal glass are represented in Table 2 ($F_{\text{tabl}} = 19.16$ and $t_{\text{tabl}} = 4.30$).

The correlation of data based on the Fisher and Student criteria revealed no systematic error, which makes the complexonometric titration method suitable for the determination of the contents of copper(II) and zinc(II) oxides in tinted crystal glass.

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